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EFFECT OF MOISTURE-CONDUCTING PROPERTIES OF CERAMIC MIXTURES ON THE PROCESS OF PLASTIC MOLDING

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The filtration, rheological and compressive properties of ceramic mixtures and their interaction are studied. Parameters for estimating the properties are suggested. It is established that the moisture-conducting properties of ceramic mixtures predetermine their molding properties, which can be affected purposefully by controlling the grain composition of the comparatively coarsely disperse skeleton of the mixture, as well as the dispersion, colloid chemical, and rheological properties of the porous suspension.

Two important problems should be solved in plastic molding of preforms of ceramic articles, namely, imparting to them the specified profile or shape and compacting them. As a rule, this can be provided in the cases when the mixtures have optimum grain compositions, colloid chemical, and rheological properties. These properties are closely interrelated and attempts to estimate the molding properties of the mixture with one of the parameters do not give reliable results, which is confirmed by works where the molding properties are estimated, for example, with only the rheological or only the deformation characteristics [1, 2].

Moistened ceramic mixtures are typical heterogeneous systems represented by a structural skeleton and a porous substance. The structural skeleton consists of relatively coarsely disperse particles and does not possess the requisite plastic properties in the case when its interparticle space is filled by a low-viscosity liquid or a low-concentrated unstructured suspension, the solid phase of which consists of particles finer (by 1 – 3 orders of magnitude) than those of the structural skeleton. Therefore, the proportion of the structural parts of the mixture and the properties of the porous

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TABLE 1

Ceramic mixture	Molding moisture content (abs.), %	Basic clay-forming minerals	Content of fraction finer than 0.005 mm, %	Atterberg plasticity, %	Flow pressure, MPa	Deformation rate, sec^{-1}	Dynamic yield strength, MPa	Nominal viscosity, Pa · sec $\times 10^{-3}$	Parameters of moldability		Maximum molecular moisture capacity, %
									$P_{m_1} \times 10^{-3}$	P_{m_2}	
Based on Rodionovskoe loam	24.0	Hydromica, montmorillonite	9.0 – 13.6	6.5 – 8.5	0.5 – 1.4	12 – 400	1.06* / 1.06	0.54 / 0.86	10.00 / 10.60	0.734	12.80
Based on Bakcharskoe clay	27.8	The same	31.8	21.2	0.6 – 1.8	8 – 400	1.05 / 1.28	1.02 / 1.50	5.92 / 4.70	0.947	14.06
	26.0		31.8	21.2	1.0 – 2.0	10 – 310	1.50	1.61	4.44	—	—
Based on Voronovskoe clay	28.0	Kaolinite, hydromica	27.2	18.5	0.3 – 1.8	10 – 400	0.69 / 0.82	2.14 / 2.41	6.66 / 3.48	0.924	18.68
From Bogashevsky plant	27.0	The same	–	18.7	0.5 – 2.6	10 – 400	0.69 / 0.88	1.93 / 3.54	5.92 / 4.00	0.936	16.64
	26.0	The same	–	18.7	0.9 – 2.6	10 – 400	1.13	4.30	3.13	–	–
From Prokop'evsky plant	25.0	–	–	18.8	0.5 – 1.4	10 – 400	0.82	1.50	3.33	0.938	16.78
	23.0	–	–	–	0.9 – 2.0	10 – 400	1.18	1.45	3.63	–	–

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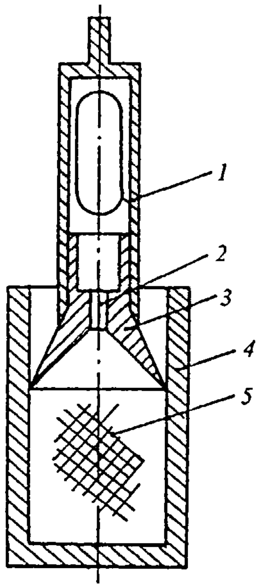

Fig. 1. Diagram of the capillary viscometer: *1*) sleeve for fixing the indentor and transferring pressure from the loading system; *2*) capillary ($l = d = 3$ mm); *3*) indicator; *4*) casing; *5*) studied mixture.

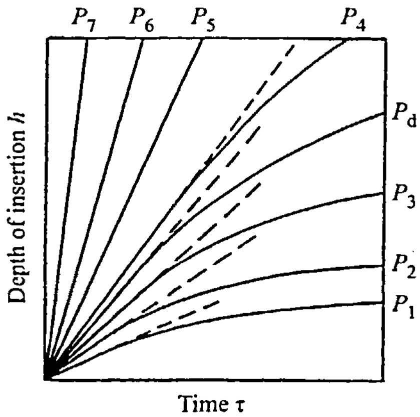

Fig. 2. Speed of indentor insertion in the casing at various stresses caused by deformation of the mixture.

substance greatly affect the molding properties. It is important that the notions of the plasticity and the moldability of a mixture are not identical and the moldability is understood as the capacity of the mixture to acquire the shape of the preform without external and internal defects under an external action.

In the volume-stressed state acquired by the mixture as a result of an external mechanical action, the liquid phase moves from more stressed regions to less stressed ones, which is the main cause of formation of the defect structure of the mixture due to local nonuniformity of the physical (density, moisture content) and rheological properties.

The semifinished product molded from such a mixture will contain a whole set of defects that manifest themselves markedly in drying and firing of the articles. The filtration properties of ceramic mixtures are virtually not considered when estimating the molding properties. However, the experience of soil specialists accumulated in soil mechanics [3] shows that a comparison of the deformation and filtration characteristics peculiar to every mixture and a study of the compression properties can give valuable results on the moldability of the mixture and methods for controlling its properties.

We studied brick clays from the Rodionovskoe and Bakcharskoe deposits (Tomsk Region) and the Voronovskoe deposit used by the Bogashevsky experimental plant of artistic ceramics for fabricating molding mixtures and cast slips, and the mixture of the Prokop'evsky porcelain plant (see Table 1).

The rheological properties of the mixtures were studied using a capillary viscometer (USSR Inventor's Certificate 667866) with a pneumatic loading system that makes it possible to create a specific pressure of up to 4 MPa and attain deformation rates of the mixture ranging between 5 and 600 sec^{-1}. The motion of the indenter is detected by a resistance gauge and a KSP-4 device. The diagram of the indenter and the casing of the capillary viscosimeter is presented in Fig. 1. The design is improved relative to the known variants since contact between the indenter and the casing occurs over a circular line and the studied mixture in the casing remains immobile; only the part which is contained in the conical bell of the indenter flows out. The specific pressure of the outflow is calculated by the formula

$$P_{fl} = \frac{F_n (\operatorname{ctan}\frac{\alpha}{2} - f)}{\pi (R^2 - r^2)},$$

where F_n is the force acting on the mixture, N; α is the angle at the vertex of the conical bell, deg; f is the friction coefficient of the mixture against the material of the indenter; R is the radius of lower base of the cone, m; r is the radius of the capillary, m.

The effect of the friction coefficient of the mixture was not taken into account in the present work.

Flow of the tested ceramic mixtures through the capillary was characterized by monotonic deceleration when the stresses in the mixture were less than or equal to the dynamic yield strength P_d (Fig. 2). This should be caused first by compaction of the solid phase of the mixture under the action of the external load and the relaxation displacement of the liquid phase that accompanies this process. Depending on the moisture-conducting properties of the mixture, the difference in its moisture contents at the beginning and end of the flow process can attain 2 – 5% and even exceed this value, which improves the mechanical properties of the mixture and decelerates its flow under the given pressure. Therefore, the evaluation of the flow rate of the mixture in terms of its mean volume flow rate is incorrect and it is expedient to use only the initial region of the dependences $h = f(\tau)$ for determining the flow rate (at $P < P_d$).

The rheological properties of the mixtures determined at the optimum molding (absolute) moisture content are presented in Fig. 3. It can be seen that 1-day aging of the mix-

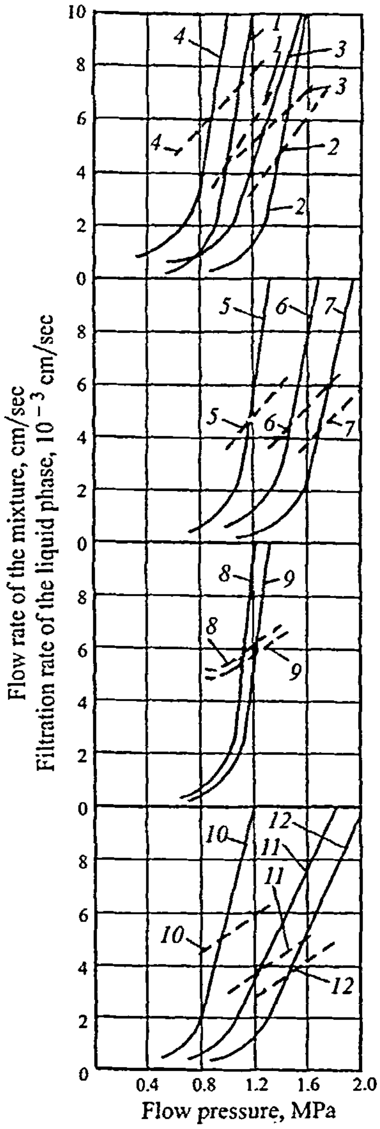

Fig. 3. Dependence of the flow rates of ceramic mixtures (solid curves) and filtration rates of the liquid phase (dash curves) on the applied pressure: *1, 2*) freshly prepared and aged mixtures based on Voronovskoe clay; *3*) porcelain mixture from the Prokop'evsky plant with a moisture content of 23%; *4*) the same with a moisture content of 12%; *5, 6*) freshly prepared and aged mixtures based on Bakcharskoe clay with a moisture content of 27.8%; *7*) aged mixture based on Bakcharskoe clay with a moisture content of 26%; *8, 9*) freshly prepared and aged mixtures based on Rodionovskoe loam; *10, 11*) freshly prepared and aged mixtures from the Bogashevsky plant with a moisture content of 27%; *12*) aged mixtures from the Bogashevsky plant with a moisture content of 16%.

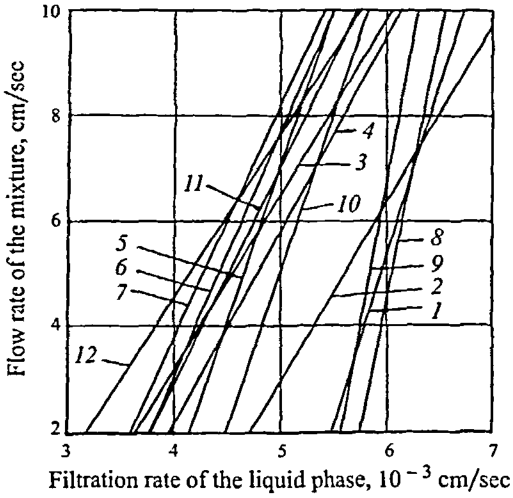

Fig. 4. Ratio of the flow rates of ceramic mixtures to the rates of filtration of the liquid phase at various stresses caused by deformation of the mixtures: *1 – 12*) the notation is as in Fig. 3.

ture increases the dynamic yield strength, and a decrease in the molding moisture content of the mixture only affects the increase in the dynamic yield strength.

The moisture-conducting properties of the mixtures were estimated from the relative rate of filtration of the liquid phase through the mixtures, for which about 10 cm^3 of the mixture was placed in a cylindrical press mold between two packets of filter paper and compressed under specific pressures corresponding to the pressure range of flow of the mixture on the rheological curve. The relative filtration rate was determined as the fraction of the moisture in a certain total moisture volume (100 cm^3) contained in the mixture and passing through the unit of area per unit of time, i.e.,

$$v_l = \frac{D \times 100}{S\tau},$$

where v_l is the relative filtration rate of the liquid phase, cm/sec; D is the fraction of the moving moisture in relative units; S is the summed area of the upper and lower bases of the cylindrical specimens of the mixture, cm^2; τ is the time of the action of the constant load, sec; $\tau = 300$ sec.

The filtration time τ of 300 sec was chosen because during this period, removal of moisture from the compressed mixture occurred according to a virtually linear dependence. The final moisture content of the mixture was determined for specimens 5 – 7 mm wide cut from a disc near the diameter.

The proportion of the moving moisture was calculated as the ratio of a specified amount of migrating moisture to the maximum possible amount of capillary-mobile water

$$D = \frac{W_i - W_f}{W_i - W_{mmm}},$$

where W_i and W_f are the initial and the final absolute moisture contents, %; W_{mmm} is the maximum molecular moisture capacity, %.

The maximum molecular moisture capacity (or the lowest capillary moisture content) was determined by the formula of A. F. Lebedev known from soil science [4]. This moisture capacity is a certain conventional limit of the quan-

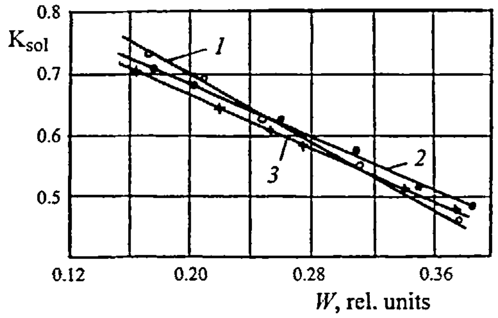

Fig. 5. Effect of the moisture content W of a mixture on the packing coefficient of its solid phase K_{sol}: *1*) mixture based on Rodionovskoe loam; *2*) mixture from the Bogashevsky plant; *3*) mixture based on Bakcharskoe clay.

titative and qualitative changes in a disperse system above which the main role in retaining the moisture belongs to capillary forces. The results obtained show that the dependences of the flow rate of the mixture and the filtration rate of the liquid phase on the stresses in the deformed mixture, which exceed the ultimate yield strength, are linearly dependent. i.e.,

$$v_{fl} = a v_{fi} - b,$$

where v_{fl} and v_{fi} are the flow rate of the mixture through the capillary (cm/sec) and the filtration rate of the liquid phase (cm/sec) under the given pressure, respectively.

Such dependences for all of the studied mixtures are presented in Fig. 4. It can be seen that in the given range of deformation stresses in the mixture above the dynamic yield strength, the ratio of the change in the flow rate of the mixture to the change in the filtration rate of the liquid phase is a constant value for the given mixture under the given conditions, i.e.,

$$P_{m_1} = \frac{\Delta v_{fl}}{\Delta v_{fi}},$$

where P_{m_1} is the moldability parameter or tangent of the slope of the straight lines in Fig. 4 to the abscissa; v_{fl} and v_{fi} are the changes in the flow rate of the mixture and the filtration rate of the liquid phase.

It follows from Table 1 and Fig. 4 that the smaller the tangent of the slope of the straight line to the abscissa or the value of P_{m_1}, the better the molding properties of the ceramic mixture. The value of P_{m_1} reacts quite delicately to the conditions of preparation of the mixture, its moisture content, composition and moisture-conducting properties. The best molding properties are exhibited by the mixture characterized by the highest difference in the filtration rates of the liquid phase in a constant interval of flow (deformation) rates. This can be provided by optimizing the ratio of the relatively coarsely disperse skeleton of the mixture to the porous substance (suspension) with a particle size below 0.005 mm.

A great effect on the molding properties of the mixtures is exerted by their viscosity. The low viscosity of the mixture based on Rodionovskoe loam does not make it possible to increase the deformation stress much above the dynamic yield strength; though the mixture has good moisture-conducting properties, the difference in the filtration rates is not great, i.e., in the given range of acting stresses, the mixture does not have enough time for compacting. The molding properties of such mixtures can be improved by increasing the amount of porous substance or by increasing the viscosity of the liquid phase by introducing the appropriate additive. If the mixture possesses too high viscosity, its molding properties will not be good, because despite the possibility of applying pressures much above the yield strength, such a mixture will have low moisture conduction and will not be compacted during the time spent in the molding machine. Quality preforms from such mixtures can be fabricated by using either leaning additives or very low deformation rates.

Thus, the main principle to be observed in plastic molding is that each deformation rate should correspond to a strictly determined filtration rate of the liquid phase. This can be provided by equipment in which the deformation rates of the mixture can be controlled continuously or at least by steps.

The opinion that compaction of the mixture in molding is realized through squeezing out of the liquid phase was confirmed by compression tests of the mixtures at various moisture contents and pressures in a mold having an opening 3 mm in diameter in the lower part of the side surface.

The mixture was compressed to a solid, virtually biphase, water-saturated state that corresponded to the static yield limit, i.e., at this pressure the mixture began to flow from the press mold (in nonplastic materials, the liquid is squeezed out). In specimens molded under these conditions we determined the total volume mass, the volume mass of only one solid phase, calculated the packing coefficient of the solid phase K_{sol}, and plotted the dependence of K_{sol} on the moisture content of the mixture (Fig. 5). We established that this dependence is linear when the moisture content of the mixture exceeds the lowest capillary moisture content, and a change in the packing coefficient of the solid phase of the mixture ΔK_{sol} corresponds to a strictly specific change in the moisture content of the mixture ΔW, which is a constant factor for the given mixture. This fundamental dependence can be used for estimating the compactibility of disperse materials or systems in pressing, pelletizing, granulating, and as a parameter for estimating the molding properties of ceramic mixtures, i.e.,

$$P_{m_2} = \frac{\Delta W}{\Delta K_{sol}}, 0 < P_{m_2} < 1.$$

The higher the value of P_{m_1}, the better the molding properties of the ceramic mixtures, because in this case the principle of adequate variation of the volume concentration of

solid phase of the system with a change in its moisture content is observed to the highest degree.

The suggested parameters make it possible to estimate the molding properties of ceramic mixtures and show ways for their improvement by acting on the deformation rate of the mixture and the rate of movement of the liquid phase. By controlling the granulometric composition of the solid phase of ceramic mixtures, the mineralogical and the colloid chemical compositions of their finest part, and the rheological properties of the liquid phase, the molding properties of the mixtures can be changed purposefully.

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